

# Critical Charge in Gapped Graphene: the role of the screening of the interaction potential by $\sigma$ -orbitals.

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Due to its unique structure, graphene provides a condensed-matter model of particle physics phenomena. One is the critical charge which is highly interested. The investigation of critical charge in gapped graphene is performed within single particle approach by means of Dirac equation integration. The screened Coulomb interaction between charged defect and graphene electron excitations is investigated. Two kinds of mass gap generation and various values of substrate dielectric permittivities are considered. It is shown that the critical charge phenomenon can be observed even with quite small charges for physically motivated parameters.

Keywords: Critical charge; Graphene; Numerical calculation.

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## Introduction

The critical charge problem is significant for modern physics. In nuclear physics this phenomenon is responsible for the instability of nuclei with charges large than some critical values [1], [2]. The fundamental reason of it is the relativistic behavior of electrons in the strong potential of a heavy nucleus. The idea of the experimental investigation of supercharges in heavy ion collision experiments was proposed many years ago [3], [4], [5]. But, after great efforts, the situation with the experimental observation of critical charge phenomenon in nuclear physics is still unclear. The first observation of the critical charge evidence was reported in [6], [7], but later experiments did not confirm the first results [8], [9], [10], [11], [12], [13]. The modern theoretical studies [14] show that electron-positron pair creation in heavy ion collisions is a more complicated process than it was expected earlier, and the possibility of the critical charge observation is still an open problem.

The phenomenon of critical charge can be considered not only in nuclear physics. The one-dimensional Coulomb problem in carbon nanotubes was considered in [17]. The critical charge has recently become possible to be explored also in two-dimensional condensed matter structures, e. g. in graphene [15], [16].

Graphene is a single layer of carbon atoms [18]. One of its most significant features is that the electron excitations are massless fermions and can be described as effective quasi-

relativistic Dirac particles. The "speed of light" is determined by the Fermi speed  $v_f$  - the speed of elementary excitation propagating, and it turns to be much smaller than the light speed in vacuum. This fact makes the studies of the quasi-relativistic phenomena in graphene much easier. Particularly, the critical charge in graphene is expected to be obtained at smaller values of  $Z$  [19], [20]. After these theoretical considerations the critical charge phenomenon has been observed experimentally [15]. The quasi-bound states of itinerant graphene electrons at supercritically charged vacancies were recently detected in graphene on the boron nitride (BN) substrate [16]. The interesting feature of this experiment stems from the fact that mass gap is generated by BN substrate. In our studies we consider a similar system.

The great progress in the study of critical charge problem in graphene can help us in the study of the critical charge problem in nuclear physics. Unfortunately, the analogy is not full due to a very essential difference: the excitations in graphene are massless particles but electrons in QED have non-zero masses. If we want to use graphene as a condensed matter model of the processes in strong electromagnetic fields in atomic physics, some mechanism of mass gap generation should be proposed.

The obtaining of gapped graphene is a very considerable problem for future nanotechnological applications. The mass gap in graphene can be induced by the sublattice symmetry breaking of the hexagonal lattice. Such a breaking can be achieved by the interaction with special substrates if one of the sublattices interacts with the substrate stronger than the another one. For example, the hexagonal boron nitride has almost the same lattice as graphene. If one places a graphene layer on the boron nitride substrate, its sublattices will be not equivalent to each other due to the difference between the interactions of carbon atoms with atoms of boron and atoms of nitrogen. This sublattice symmetry breaking produces the mass gap about 53 meV [21]. Another prospective possibility to produce the gapped graphene was proposed in [22]. In this case substrate is SiC but graphene layers are epitaxially grown on this SiC substrate. It was shown that the mass gap about 0.26 eV is produced in this case. Moreover, the mass gap can be opened in case of the absorbtion of hydrogen on the graphene layer [23] or due to finite size effects (in nano-ribbons and so on).

In the present study we investigate the critical charge phenomenon in gapped graphene and try to estimate the critical charge value. The two-dimentional Coulomb problem without screening was studied in framework of Dirac equation formalism [24] and in framework of the tight-binding lattice model [25]. In [26], [27] the phenomenologically regularized Coulomb problem was studied. In this paper we apply the effective potential of the interaction between a charged defect and electron excitations, considering the  $\sigma$ -orbital screening [28], [29]. It is well known that the critical charge phenomenon is very sensitive to the details of the potential near the position of the charge. So one can predict that the value of the critical charge should be strongly dependent of regularization of singular Coulomb potential near the

origin. The  $\sigma$ -orbital screening plays the role of the physical regularization in this problem. We investigate the role of this  $\sigma$ -orbital screening in this paper.

# 1. The Dirac Equation of Gapped Graphene with Screened potential

Graphene is a two-dimensional material consisting of a hexagonal (also called honeycomb) lattice of carbon atoms. Three of its four valent electrons provide the chemical bonds in this lattice ( $\sigma$ -orbitals). The fourth one is valent and it provides the electronic properties of graphene. The theory of solids predicted for the excitations associated with electron tunnelling between lattice sites to be massless Dirac particles. Later the mass of the excitation turned up to depend on the substrate the graphene sample placed on. For example, Graphene on  $\text{SiO}_2$  substrate is described by two-dimensional Dirac equation for massless particles and graphene on SiC substrate is described by Dirac equation for massive particles. The effective mass of these particles is determined by energy gap  $G = mv_f^2$ . The value of mass gap is determined by substrate, it is associated with sublattice symmetry breaking.  $v_f$  is Fermi velocity, an analogue of speed of light for excitations in graphene. The value of Fermi velocity is  $v_f \approx c/300$ . We represent the excitations as two-dimensional Dirac particles with charge  $e$  interacting with three-dimensional Coulomb field of defect with charge  $Ze$ . The Dirac equation for such particles is

$$\left( -i\hbar v_f (\sigma_x \partial_x + \sigma_y \partial_y) - \frac{1}{\varepsilon_{eff}} \left( \frac{Ze^2}{r+a} \right) + G\sigma_z \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (1)$$

Here

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2)$$

are Pauli matrices. The effective dielectric permittivity is  $\varepsilon_{eff} = (\varepsilon + 1)/2$ , where  $\varepsilon$  is the dielectric permittivity of the substrate. This expression is motivated by the fact that the substrate is in only one half-space from the graphene sheet, and there is vacuum ( $\varepsilon = 1$ ) in the other half-space. The exact form of this expression is strictly proved in classical electrodynamics with the method of mirror charges [30]. ( $\varepsilon = 4$  for  $\text{SiO}_2$  substrate and  $\varepsilon = 10$  for SiC substrate). The potential is screened by  $\sigma$ -orbitals. Fig. 1 represents the screened Coulomb potential approximation for  $a = 0.12\text{nm}$  and values of the potential obtained from more detailed condensed matter calculations in [28], [29]. One can see that the approximation is acceptable.

The critical charge problem in a similar (screened Coulomb) one-dimensional potential has been studied theoretically [31], [32], [33].

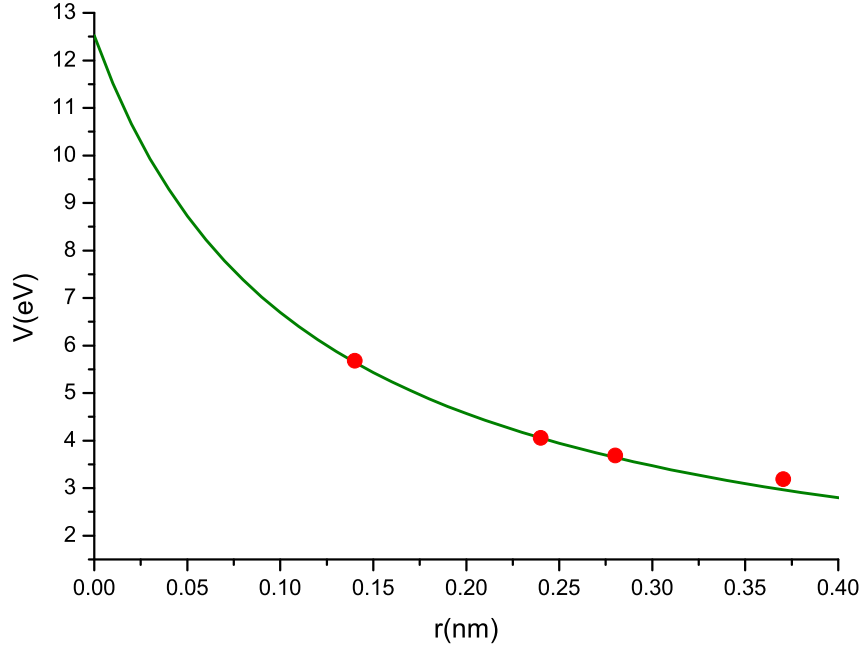


Figure 1: Screened potential for screening parameter  $a = 0.12$  nm (green line) and potential obtained by detailed calculation by Wehling et al. (red dots).

We explore the ground state near a charged defect. The experiments on critical charge in graphene use charged ions placed on its surface as such defects. These ions were discovered to form a non-trivial distribution of electron-hole pairs. It confirms that even a small charge is sufficient to be critical in this system. We apply a quite simple theoretical model to describe the critical charge in graphene placed on a substrate generating a mass gap. This formulation of the problem resembles the one for critical charge of atomic nuclei.

The equation (1) can be solved with the substitution

$$\psi_j(r, \phi) = \frac{1}{\sqrt{r}} \begin{pmatrix} e^{-i(j-1/2)\phi} A(r) \\ ie^{-i(j+1/2)\phi} B(r) \end{pmatrix}, \quad (3)$$

where  $j$  is the total angular momentum of the state.

We obtain a system of differential equations that provides the solution for radial part

$$\begin{bmatrix} \left( E + \frac{1}{\varepsilon_{eff}} \left( \frac{Ze^2}{r+a} \right) - G \right) & -\hbar v_f \left( \partial_r + \frac{i}{r} \right) \\ \hbar v_f \left( \partial_r - \frac{i}{r} \right) & \left( E + \frac{1}{\varepsilon_{eff}} \left( \frac{Ze^2}{r+a} \right) + G \right) \end{bmatrix} \begin{bmatrix} A(r) \\ B(r) \end{bmatrix} = 0. \quad (4)$$

We consider the ground state (s-wave) electron ( $j=1/2$ ). The Dirac equation for this case is solved by shooting method. The performance, accuracy and even correctness of such algorithms strongly depend both on the physical parameters of the system and on the

parameters of the algorithm. In order to control all of these effects we used an own written program for numerical calculations.

Idea of the shooting method is numerical integration of differential equation from zero and from infinity and stitching the solutions at some middle point. Asymptotic behavior of the correct solutions is  $A(r), B(r) \sim \sqrt{r}$  at  $r \rightarrow 0$  and  $A(r), B(r) \sim e^{-\kappa r}$  at  $r \rightarrow \infty$ . Corresponding boundary conditions in zero are set by hand. To obtain the required asymptotic at infinity it is enough to start shooting from arbitrary (small) value of function at arbitrary (large) value of radius, than the correct solution exponentially increases and the incorrect one exponentially decreases.

The integration of the equation was performed by RK4 method. The criterion of correct (smooth) stitching is  $W(E) = A_l A'_r - A_r A'_l \rightarrow 0$  (the similar expressions as for  $A(r)$  are suggested everywhere for  $B(r)$ ). Here indices  $l$  and  $r$  stand for left (shooting from zero) and right (shooting from infinity) solutions in the stitching point for given energy. This equation was solved with the accuracy  $10^{-6}$  for  $E$ .

To control that the stitching is really smooth we also used a criterion  $(A_l A'_r - A_r A'_l)/(A_l A'_r + A_r A'_l) \ll 10^{-3}$ .

The numerical solution is closer to the physical one for smaller discretization step  $d$  and larger "infinity"  $R_\infty$  (the maximum value of radius, a point where the boundary conditions for infinity are set). We suggested that the numerical solution is sufficiently close to the continuous one if 10 times smaller  $d$  and 10 times larger  $R_\infty$  does not significantly change it.

Another criterion of the correctness of the solution is based on the exponential decay of the bound state wavefunction: we suggested that the numerical solution is correct if  $|\overline{A(r)}|_{[0.9R_\infty; R_\infty]}/\max A(r)_{[0; R_\infty]} \ll 10^{-3}$ .

The solution provides the ground state wavefunction and energy level for the equation (4). We examine the energy level inside the mass gap  $-G < E < G$  as a function of the charge of the defect and the dielectric permittivity of substrates  $\varepsilon$ .

## 2. Critical charge in gapped graphene for screened potential model

The equation (4) was solved as an eigenvalue problem to obtain the spectrum energy levels  $E_i$  and corresponding wavefunction. In fact we need only the ground state energy level  $E_0$  to determine the critical charge. The spectrum was obtained for various values of defect charge  $Ze$  and the dielectric permittivity of substrates  $\varepsilon$ , the calculations were performed for a value of parameters  $a = 0.12$  nm (screening length in potential) and  $G = mv_f^2$  (mass gap, i.e. excitation effective mass).

At large value of the dielectric permittivity of the substrate the potential of interaction

between the defect and the electron excitation is decreased by the influence of the substrate and all the energy levels, including the ground state one, asymptotically go to  $+G$ . The energy levels decrease if the dielectric permittivity of the substrate becomes smaller. The decrease of ground state energy to  $-G$  corresponds to the critical charge  $Z_{cr}$  – at these values of defect charge and the dielectric permittivity of the substrate the energy production of the electron-hole pair is equals to zero and our system becomes unstable. Physically it leads to production of the the electron-hole pairs and to practically screening of the critical charge of defect by the cloud of inverse charges. This process could lead to the generation of "additional" electrons and to changing of the local density of states which can be detected experientially and can be interpreted as a signal of the critical charge achievement.

In our work the two type of experimental situation are studied. Let us consider the defects with different integer value of charge ( $Z=1, 2, 3, 4, 5$ ) placed on the graphene sheet. For the generation of mass gap the special type of the substrate must be used. As we discussed in the previous section there are two types of substrate that can break the sublattice symmetry of graphene and generate the mass gap in this system. One of them is the single layer boron nitride (BN) on the ( $\text{SiO}_2$ ) substrate and another is barrier graphene layer on silicon carbide (SiC) substrate. Let us consider each of these situations.

The experimental scheme for the BN-SiO<sub>2</sub> system is shown in the Fig. 2. The dielectric permittivity of SiO<sub>2</sub> is 3.9. The difference of boron-carbon nitrogen-carbon interactions generates the mass gap for electron excitations in graphene about  $G = 0.053\text{eV}$ . The results of numerical simulation of this system for different values of the defect charge and of the substrate dielectric permittivity are shown in the Fig. 2.

One can see that for BN-SiO<sub>2</sub> system the charges 3 and more are super-critical, and the charge 3 is very close to the critical value.

The experimental scheme for the barrier graphene-SiC system is shown in the Fig. 3. The dielectric permittivity of SiC is about 10. As the upper graphene layer is in AB-structure with the barrier graphene layer, one of the sublattices of the layers is in strong interaction while the other is not. This is a strong sublattice symmetry breaking that generates a mass gap of about  $G = 0.26\text{ eV}$ . The results of numerical simulation of this system for different values of the defect charge and of the substrate dielectric permittivity are shown in the Fig. 3.

The simulation shows that for barrier graphene-SiC system the charges 5 and more are super-critical; and the charge 4 and less are sub-critical.

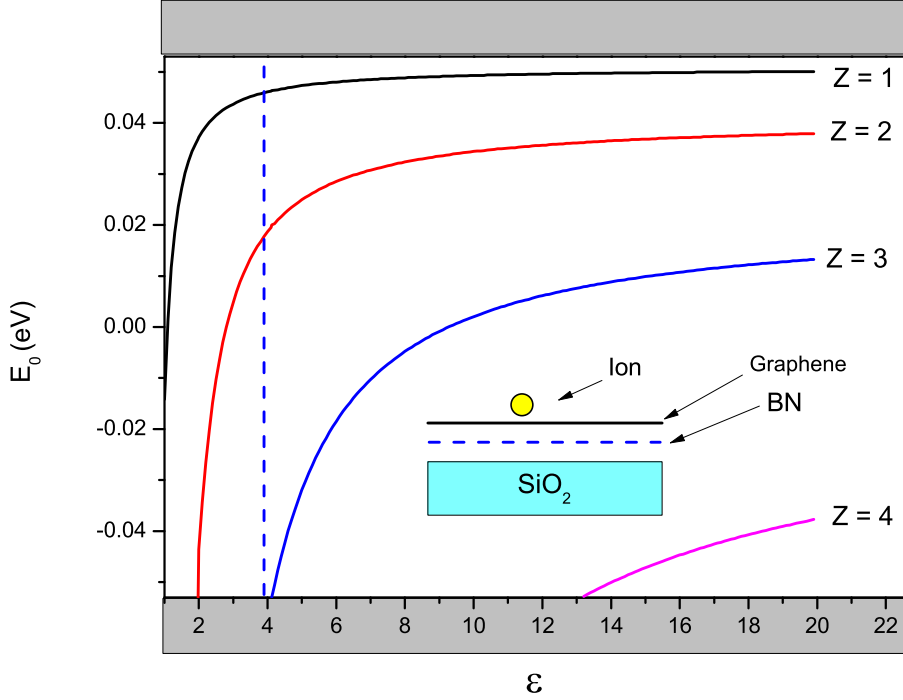


Figure 2: Ground state energy as a function of the substrate dielectric permittivity  $\epsilon$  for different charges of the defect. Mass gap is  $G = 0.053$  eV (boron nitride). The dashed line corresponds to the dielectric permittivity of  $\text{SiO}_2$ .

### 3. Conclusions

The main goal of our work is to study the critical charge effect in the gapped graphene. We have investigated the influence of the  $\sigma$ -orbitals screening on this phenomenon. It is well known that the critical charge value is very sensitive to the behavior of the interaction potential near the charge. Due to this fact one could expect that the parameters of screening are crucial for this problem.

The recent experiment [16] has shown that the external charge vacancy in graphene can form the artificial atom with electrons of conductivity. It was shown that the transition to the supercritical regime can be observed in this experiment by the study of the density of state peaks below the Dirac point energy. These peaks are associated with quasi-bound states localized near the charge vacancies so they are the clear signal of the transition into the supercritical regime.

It is very well known that the supercritical charge effect is very sensitive to the behavior of the potentials at a short distance to the charge. The great success in the experimental study of the supercharge phenomenon in graphene opens the possibility of the direct investigation of short distance effects in graphene such as the Coulomb potential screening, the influence

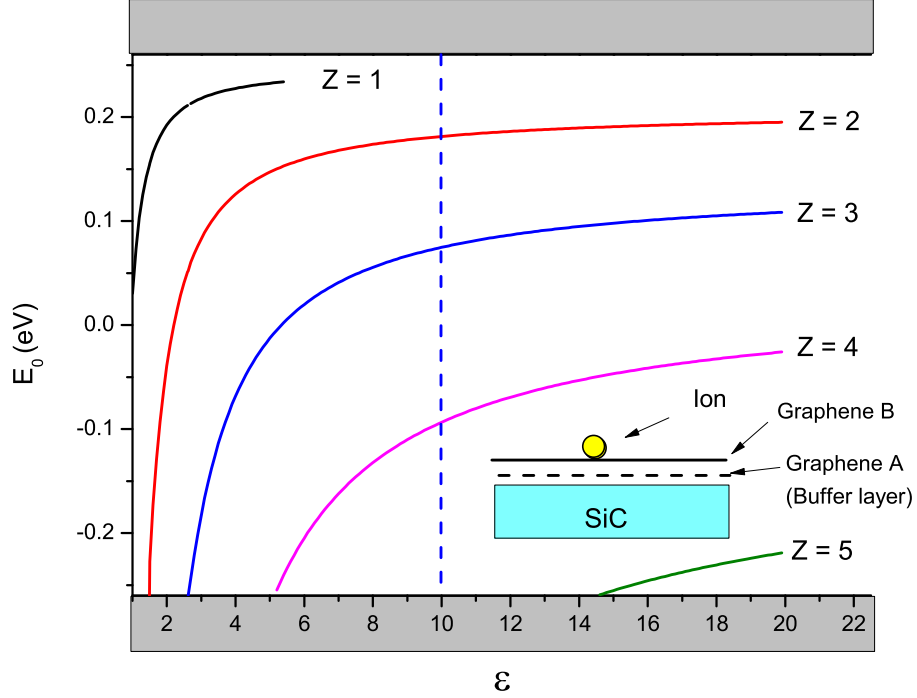


Figure 3: Ground state energy as a function of the substrate dielectric permittivity  $\epsilon$  for different charges of the defect. Mass gap is  $G = 0.26$  eV (barrier graphene layer). The dashed line corresponds to the dielectric permittivity of SiC.

of the dielectric properties of the substrate, the effects of graphene sheet deformation, and so on. In our study we have investigated the influence of the  $\sigma$ -orbital screening of Coulomb potential on the critical charge effect in the cases of two very popular gapped graphene systems: graphene on the BN-SiO<sub>2</sub> substrate and graphene on barrier graphene-SiC substrate.

In our work we used the 2+1-dimensional Dirac equation for the study of the excitation in graphene in strong external potential of a point charge. Based on the [28], [29] the potential was suggested to be Coulomb screened. This screening was obtained in the framework of the effective extended Hubbard model of graphene by using of determinant quantum Monte Carlo (DQMC) method. The screening of Coulomb potential was also studied in [34] in framework of the Thomas-Fermi method. This approximation method is very well applicable for a wide range of radius values, and the resulting form of screening differs from DQMC prediction we used in our work. We plan to investigate a similar problem also for this form of potential in our future studies. The comparison of the results with the experimental data can provide the most optimal form of the approximation of Coulomb potential at short distances.

Dirac equation was solved numerically by the shooting method. We have investigated two physical situations: graphene on the BN-SiO<sub>2</sub> substrate and graphene on barrier graphene-SiC substrate. The numerical simulations have shown that the values of critical charge are



3 and 5 respectively.

We also investigate how the substrate dielectric permittivity does influence on the critical charge phenomenon. For any physical ( $\varepsilon > 1$ ) situation the critical charge is larger than 1. This conclusion is in agreement with the experimental data [16].

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